



TITLE:

Studies on Lactone Formation in Vapor Phase. (III) : Mechanism of Lactone Formation from Diols

AUTHOR(S):

Oka, Shinzaburo

CITATION:

Oka, Shinzaburo. Studies on Lactone Formation in Vapor Phase. (III) : Mechanism of Lactone Formation from Diols. Bulletin of the Institute for Chemical Research, Kyoto University 1963, 41(2-4): 221-221

ISSUE DATE:

1963-10-15

URL:

<http://hdl.handle.net/2433/75960>

RIGHT:

Studies on Lactone Formation in Vapor Phase. (II)

Synthesis of ϵ -Caprolactone

Shinzaburo OKA

Bulletin of the Chemical Society of Japan, 35, 562 (1962)

Dehydrogenation of 1,6-hexanediol to ϵ -caprolactone with numerous mixed catalysts has been studied. Attempts to dehydrogenate 1,6-hexanediol with copper-zinc oxide or copper-magnesium oxide catalyst, which gave γ -butyrolactone and δ -valerolactone in good yields, were unsuccessful. The most favorable catalyst giving ϵ -caprolactone in 68% yield, had the composition of $\text{CuO}:\text{Cr}_2\text{O}_3:\text{ZnO}=2:0.5:1$. The catalysts which contained one of the components excessively lowered both the activity and selectivity. Preparation of 1,6-hexanediol, the starting material for ϵ -caprolactone, was performed as follows, and the reaction conditions of each step have been examined.

- 1) $\text{CH}\equiv\text{CH}+\text{HCHO}\longrightarrow\text{CH}\equiv\text{CCH}_2\text{OH}$
- 2) $2\text{CH}\equiv\text{CCH}_2\text{OH}+1/2\text{O}_2\longrightarrow\text{HOCH}_2\text{C}\equiv\text{CC}\equiv\text{CCH}_2\text{OH}+\text{H}_2\text{O}$
- 3) $\text{HOCH}_2\text{C}\equiv\text{CC}\equiv\text{CCH}_2\text{OH}+4\text{H}_2\longrightarrow\text{HO}(\text{CH}_2)_6\text{OH}$

Studies on Lactone Formation in Vapor Phase. (III)

Mechanism of Lactone Formation from Diols

Shinzaburo OKA

Bulletin of the Chemical Society of Japan, 35, 987 (1962)

To clarify the mechanism of lactone formation from diols, the behavior of dialdehydes or oxyaldehydes over the copper catalysts has been studied. With all the catalysts used, it was ascertained that the oxyaldehydes gave the corresponding lactones as easily as the diols did. On the contrary, the dialdehydes examined gave no lactones, and they were recovered up to 70% except in the case of adipaldehyde. From these experimental results, it is concluded that this reaction does not take place by an internal Cannizzaro type reaction of dialdehydes but by an intramolecular acetalization of oxyaldehydes, followed by a dehydrogenation to lactones.